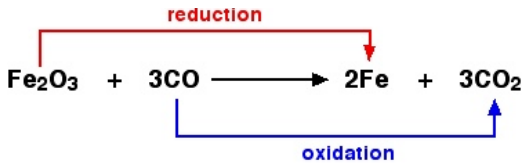
6.1 Oxidation and Reduction

Redox reactions

1) *Oxidation* is:
   i. gain of oxygen
   ii. loss of hydrogen
   iii. loss of electrons
   iv. increase in oxidation number

2) *Reduction* is:
   i. gain of hydrogen
   ii. loss of oxygen
   iii. gain of electrons
   iv. decrease in oxidation number

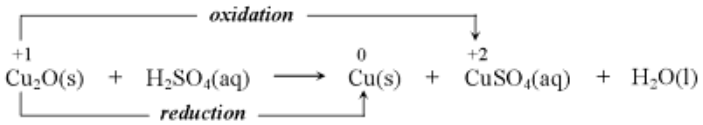
3) Oxidation and reduction always occur simultaneously in a chemical reaction. Such reaction is called a **redox reaction**. In a redox reaction, one substance must be oxidised and another must be reduced.



4) i. An *oxidising agent* is a substance which oxidises another substance and **itself is reduced**.
   ii. A *reducing agent* is a substance which reduces another substance and **itself is oxidised**.

5) In short, an oxidising agent undergoes reduction while a reducing agent undergoes oxidation.

6) **Disproportionation** is a redox reaction in which both oxidation and reduction occurs on the same atom. The atom is simultaneously oxidised and reduced.



Oxidation state (oxidation number) of a substance

1) Oxidation state shows that total number of electrons which have been removed from or added to **an element** to get to its present state.

2) i. When electrons have been removed, the oxidation number increases.(positive)
ii. When electrons have been added, the oxidation number decreases.(negative)

3) i. Since removing electrons is an oxidation process, therefore oxidation is the increase in oxidation number
ii. Since adding electrons is a reduction process, therefore reduction is the decrease in oxidation number.

3) For example, from V to V^{2+}, two electrons have been removed, therefore the oxidation state of is +2. From V to V^{3+}, three electrons have been removed, therefore the oxidation state is +3. Removing another electron gives:

$$V^{3+} + H_2O \rightarrow VO^{2+} + 2H^+ + e^-$$

Four electrons have been removed starting from V, therefore the oxidation state is +4. In all cases, V has been oxidised.

4) Another example, from S to S^{2-}, two electrons have been added, therefore the oxidation state is -2. S is said to have been reduced.

Rules to determine oxidation numbers of a substance

1) All atoms in an atom, molecule or ion can be given an oxidation number.

2) The rules to determine the oxidation number of a substance:
i. All **free atoms** in elements have an oxidation number of **zero**.
e.g. $\overset{0}{Mg}$ $\overset{0}{Fe}$ $\overset{0}{O_2}$ $\overset{0}{H_2}$ $\overset{0}{P_4}$ $\overset{0}{Cl_2}$

ii. For **simple ions**, the oxidation number is the same as the **charge** on the ion.
e.g. $\overset{+1}{Na^+}$ $\overset{+3}{Al^{3+}}$ $\overset{+2}{Mg^{2+}}$ $\overset{-2}{O^{2-}}$ $\overset{-2}{S^{2-}}$ $\overset{-1}{Cl^-}$

iii. For **polyatomic ion**, the **sum** of all the oxidation numbers of the atoms in the ion is equal to the **charge** of the ion.

e.g. MnO_4^- : $\therefore 1(+7) + 4(-2) = -1$

$Cr_2O_7^{2-}$: $\therefore 2(+6) + 7(-2) = -2$

NO_2^+ : $\therefore 1(+5) + 2(-2) = +1$

iv. For a **neutral covalent molecule**, the sum of all the oxidation numbers of the atoms in the molecule is equal to **zero**.

e.g. $\overset{+1\ -2}{H_2O}$ $\overset{+6\ -2}{SO_3}$ $\overset{+1\ -1}{HCl}$

Also, the more electronegative atom is always given a negative oxidation number while the less electronegative atom is given a positive one.

v. For **Group I and Group II elements**, their oxidation number are always +1 and +2 respectively. For aluminium, it is always +3.

vi. For **hydrogen**, its oxidation number is always +1 except in metal hydrides. For example, NaH, where its oxidation number is -1.

vii. For **oxygen**, its oxidation number is always -2 except in peroxides and fluorine compounds. For example, BaO_2, where its oxidation number is -1.

viii. For **fluorine**, its oxidation number is always -1, with no exceptions.

3) A summary:

Element	*Oxidation No.*	*Exceptions*
Group I	+1	–
Group II	+2	–
Aluminium	+3	–
Fluorine	–1	–
Oxygen	–2	–1 in *peroxides* (e.g. H_2O_2) and +2 in OF_2
Hydrogen	+1	–1 in *metal hydrides* (e.g. Na^+H^-)

4) To work out the oxidation number of a particular atom in a molecule/ ion, find the sum of all the oxidation number of the atoms present and equate it to zero/ charge of the ion. An example:

To calculate the oxidation number of Mn in $MnO(OH)_2$, MnO_4^{2-} and Mn_2O_7.

Let the oxidation number of Mn be x.

In $MnO(OH)_2$: $x + (-2) + 2(-1) = 0 \Rightarrow x = +4$

In MnO_4^{2-} : $x + 4(-2) = -2 \Rightarrow x = +6$

In Mn_2O_7 : $2x + 7(-2) = 0 \Rightarrow x = +7$

Balancing redox equations

1) There are two methods to balance complicated redox equations:
   i. Using electron half-equations.
   ii. Using changes in oxidation number.

2) **Using electron half-equations**:
   i. In this method, the redox equation is divided into two half-equations. One for oxidation and another for reduction.
   ii. Steps(**in acidic condition**):
   - Divide the equation or information given into two half-equations.
   - Balance all other elements other than oxygen and hydrogen.
   - Balance the oxygen by adding H_2O to the appropriate side of the equation.
   - Balance the hydrogen by adding H^+ to the appropriate side of the equation.
   - Balance the charge by adding electrons to the appropriate side of the equation.
   - Combine two half-equations such that the electrons cancel out each other.
   iii. An example:
   Q: Balance and complete this equation:

$$Cr_2O_7^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+}$$

   A: 1) Divide into two equations:

$Cr_2O_7^{2-} \rightarrow Cr^{3+}$.....reduction

$Fe^{2+} \rightarrow Fe^{3+}$.....oxidation

   2) Balance the atoms:

$Cr_2O_7^{2-} \rightarrow \mathbf{2}Cr^{3+}$

$Fe^{2+} \rightarrow Fe^{3+}$

   3) Balance the oxygen:

$Cr_2O_7^{2-} \rightarrow 2Cr^{3+} \mathbf{+ 7H_2O}$

$Fe^{2+} \rightarrow Fe^{3+}$

   4) Balance the hydrogen:

$Cr_2O_7^{2-} \mathbf{+14H^+} \rightarrow 2Cr^{3+} + 7H_2O$

$Fe^{2+} \rightarrow Fe^{3+}$

   5) Balance the charge:

$Cr_2O_7^{2-} + 14H^+ \mathbf{+ 6e^-} \rightarrow 2Cr^{3+} + 7H_2O$

$Fe^{2+} \rightarrow Fe^{3+} \mathbf{+ e^-}$

6) Cancel the electrons and combine the equations:

[$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$] x 1

[$Fe^{2+} \rightarrow Fe^{3+} + e^-$] x 6

the combine....

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

\+ $6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^-$

$Cr_2O_7^{2-} + 14H^+ + 6e^- + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+} + 6e^-$

same number of electrons on both sides, cancel it....

$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$

is the final answer.

iv. Steps(**in alkaline condition**):

- Balance the equation as if it happens in an acidic condition first.
- Add OH^- to both sides of the equation to react with all the H^+ to form H_2O.
- Cancel the excess H_2O on either side of the equation.

Note: If it is obvious enough that OH^- must be added in order to balance the equation, then add OH^- instead.

3) **Using changes in oxidation number**:

i. This method utilises the fact that an increase in certain amount of oxidation number in a substance must be accompanied by a decrease in same amount of oxidation number in another substance.

ii. An example:

Q: Balance and complete this equation:

$Cr_2O_7^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+}$

A: 1) Calculate the changes in oxidation number:

For Cr: +6 to +3, change is -3

For Fe: +2 to +3, change is +1

2) Balance the changes:

For Cr: -3(1) = -3

For Fe: +1(3) = +3

$1Cr_2O_7^{2-} + 3Fe^{2+} \rightarrow 1Cr^{3+} + 3Fe^{3+}$

3) Multiply everything by 2 except $Cr_2O_7^{2-}$ because there are already two atoms of chromium inside it.

$Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+}$

4) Balance the oxygen and hydrogen:

$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$ is the final answer.

Systematic names of compounds

$FeCl_2$: Iron (II) chloride: ox. no. of 2 Cl atoms is -2 and $FeCl_2$ has overall no charge - ox. no. of Fe is +2

$HClO_4$: Chloric (VII) acid: ox. no. of H is +1, 4 O atoms is -8 and $HClO_4$ has overall no charge so ox. no. of Cl is +7

NO_2: Nitrogen (IV) oxide: ox. no. of 2 O atoms is -4 and NO_2 has overall no charge so ox. no. of N is +4

$Mg(NO_3)_2$: Magnesium nitrate: this is a salt of the common acid, so they are named without including the ox. no. of the non-metal

K_2SO_4: Potassium sulfate: this is a salt of the common acid, so they are named without including the ox. no. of the non-metal

ClO_3^-: Chlorate (v) ions: the chlorine atom has a oxidation state +5

Ion	Name	Ion	Name
NH_4^+	ammonium	IO_4^-	periodate
NO_2^-	nitrite	$C_2H_3O_2^-$	acetate
NO_3^-	nitrate	$H_2PO_4^-$	dihydrogen phosphate
HSO_4^-	hydrogen sulfate	CO_3^{2-}	carbonate
OH^-	hydroxide	SO_3^{2-}	sulfite
CN^-	cyanide	SO_4^{2-}	sulfate
MnO_4^-	permanganate	$S_2O_3^{2-}$	thiosulfate
HCO_3^-	hydrogen carbonate	O_2^{2-}	peroxide
ClO^-	hypochlorite	CrO_4^{2-}	chromate
ClO_2^-	chlorite	$Cr_2O_7^{2-}$	dichromate
ClO_3^-	chlorate	HPO_4^{2-}	hydrogen phosphate
ClO_4^-	perchlorate	PO_4^{3-}	phosphate
BrO_3^-	bromate	AsO_4^{3-}	arsenate
IO_3^-	iodate		

Writing ionic equations

15 a Write an equation to show potassium hydroxide dissolving in water.

b Write an equation for liquid nitric acid dissolving in water.

c Write ionic equations for:

i the reaction in aqueous solution between sodium hydroxide and nitric acid

ii the reaction in aqueous solution between potassium hydroxide and hydrochloric acid.

a $KOH(s) + aq \rightarrow K^+(aq) + OH^-(aq)$

b $HNO_3(l) + aq \rightarrow NO_3^-(aq) + H^+(aq)$

$NaOH\ (aq) + HNO_3\ (aq) \rightarrow NaNO_3\ (aq) + H_2O\ (l)$

$Na^+\ (aq) + OH^-\ (aq) + H^+\ (aq) + NO_3^-\ (aq) \rightarrow$
$Na^+\ (aq) + NO_3^-\ (aq) + H_2O\ (l)$

$OH^-\ (aq) + H^+\ (aq) \rightarrow H_2O\ (l)$

$HCl(aq) + KOH(aq) \rightarrow KCl(aq) + H_2O(l)$

$(H^+ + Cl^-) + (K^+ + OH^-) \rightarrow K^+ + Cl^- + H_2O$

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$